平成７年度研究報告書

（プロジェクト２年度）

1996
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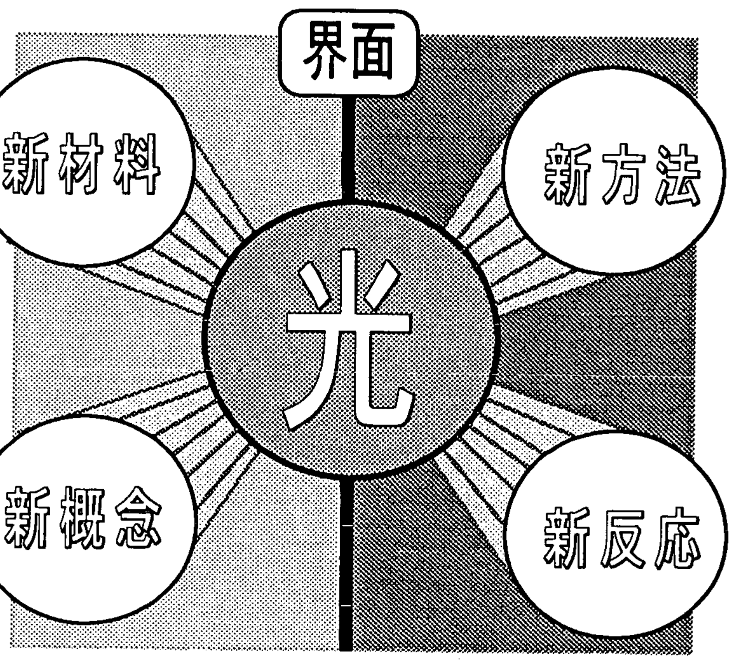

（財）神奈川科学技術アカデミー

橋本「光機能変換材料」プロジェクト

平成８年６月

Highly Transparent and Photoactive TiO_2 Thin Film Coated on Glass Substrate

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Introduction

In recent years there have been remarkable advances in TiO_2 photocatalysis research. Various applications of the photocatalytic reaction to environmental purification have been demonstrated. Most of them were on purification of air and water by using strong oxidation power of TiO_2 photocatalyst under strong UV light irradiation. Our strategies are to develop highly efficient TiO_2 thin films coated on various building materials and to apply them to decompose very small amount of pollutant in a living space (odor, bacteria, spot) under very weak UV light irradiation like room light.[1)2)]

Here, we will report a highly transparent TiO_2 thin film coated on a glass with highly photocatalytic activity, which might be practically applicable to window and glassware. These TiO_2 coated glasses are expected to have deodorizing, anti-bacterial, and anti-fouling functions.

Experimental

The present transparent TiO_2 thin film is prepared by the pyrosol process, which is the kind of chemical vapor deposition (CVD). Figure 1 shows schematic diagram of this process. As glass substrates (100mm x 50mm), quartz, soda lime glass (SLG), and SiO_2-precoated SLG (SiO_2/SLG) were used. The SiO_2 layer of the SiO_2/SLG was coated by sol-gel method with 0.1μm thickness. Source reagent for pyrolysis was titanium tetraisopropoxide in organic solvent The alkoxide solution was introduced in an ultrasonic atomizer. The atomized mist was carried by air flow into an electric furnace in which the temperature was set at 400-500°C. TiO_2 thin film was deposited on the heated glass substrates through pyrolysis of the atomized mist. The film thickness was controlled by the pyrolysis time. The photocatalytic activity of the film was evaluated by the decomposition of gaseous acetaldehyde under black light blue (BLB) irradiation. The UV light (300-400nm) flux at the TiO_2 film was 1.2mW/cm^2. Saturated gaseous acetaldehyde was injected into a 1.5L Pyrex reaction glass vessel. The irradiation was conducted at room temperature after the adsorption equilibrium was reached (ca.30min). The similar experiments using commercially available TiO_2 powder (Degussa P-25, Nippon Aerosil Co. Ltd.), Which is one of the most efficient photocatalysts were also carried out. In this case, ca.1.0g of the powder was spread uniformly over a glass substrate with the same area (100mm x 50mm)

The surface morphology of the films was analyzed by TEM and SEM, and their crystal structures by XRD and electron diffraction (ED). Depth profile of sodium was measured on an ESCA with ion spattering technique. The optical property was recorded on a UV-Vis spectrophotometer.

Results and discussion

Figure 2 shows photographs of a TiO_2-coated SLG and an SLG substrate itself. The TiO_2-coated SLG looks as transparent as the SLG. The thickness of TiO_2 layer was controlled to be 0.5-3.5 μm. The XRD and ED data showed that the TiO_2 film has a anatase structure. The particle size observed by TEM was about 10nm diameter without necking. Figure 3 shows UV-Vis transmission spectrum of the TiO_2-coated quartz. The transmittance was about 80% over the visible light region.

Figure 4 shows the photodegradation of gaseous acetaldehyde by the TiO_2 thin films on quartz, SLG, and SiO_2/SLG. The TiO_2-coated quartz showed a high photocatalytic activity. The catalytic activity of the TiO_2-coated SLG was, however, much lower than that of the TiO_2-coated quartz, although both were prepared in the similar manner. Additional feature was that the catalytic activity of the TiO_2-coated SLG increased with the increasing pyrolysis time, i.e., the increasing thickness the deposited TiO_2 layer. However, when the SiO_2/ SLG was used as a substrate instead of the bare SLG, the catalytic activity of the TiO_2-coated SiO_2/SLG became almost the same as that of the TiO_2-coated quartz. These results suggest that Na in SLG might diffuse into the deposited TiO_2 layer during pyrolysis to form inactive titanate like $NaTiO_3$, which would behave as recombination centers of electrons and holes (Fig. 5(A)). Actually, appreciable amount of Na was detected by ESCA after the TiO_2 layer on the SLG was sputtered by 20nm depth with Ar ion, while little amount of Na was found on the TiO_2 surface. However little amount of Na in the TiO_2 layer on the SiO_2/SLG was detected even after Ar ion sputtering, indicating that Na diffusion was blocked by the precoated SiO_2 layer as shown in Fig 5(B).

The 60min pyrolysis under the present condition was required in terms of TiO_2 thickness for significant catalytic activity (Fig. 6). The precoating of SiO_2 layer did not influence the transparency after TiO_2 deposition, so that the TiO_2-coated SiO_2/SLG also showed about 80% transparent in visible region (Fig. 7). Figure 8 shows the photodegradation of acetaldehyde when the TiO_2-coated SiO_2/SLG was irradiated from the front and the reverse sides. The photoactivity of the TiO_2 thin film was as higt as that of P-25, where a glass substrate with the same area was covered with mach large amount of P-25 powder. Even under irradiation of the reverse side, very high catalytic activity was revealed. The weight of TiO_2- coated glass was fewer than that of P-25 powder on. Nevertheless, The photoactivity of TiO_2-coated glass was similar to that of P-25. This implies that the TiO_2-SiO_2/SLG is applicable for window glasses, utilizing sun light as well as room light.

The present study showed that a highly transparent TiO_2 photocatalytic thin film can be coated on a glass by pyrosol process. This material has an enough hardness and abrasion resistance for its practical application.

References

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2) T. Watanabe, A.Kitamura, E. Kojima, C. Nakayama, K. Hashimoto, A. Fujishima, "Photocatalytic Purification and Treatment of Water and Air", Ed., D.E.Ollis, H. Al-ekabi, Elsivierb (1993), p747.

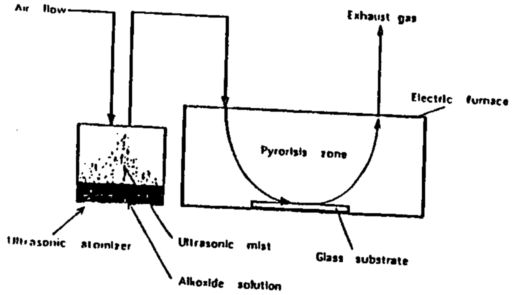

Figure 1 Schematic diagram of the pyrosol process for preparation of TiO_2 thin film.

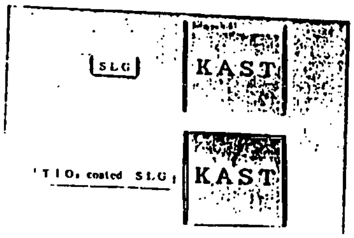

Figure 2 Photograph of TiO_2 coated SLG, and the SLG substrate.

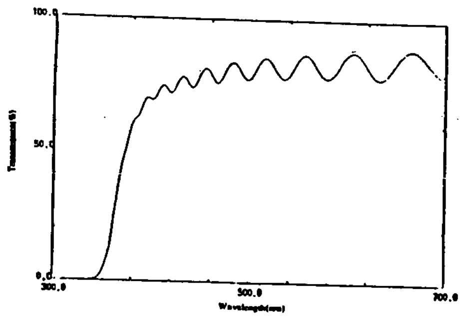

Figure 3 UV-Vis transmission spectrum of TiO_2 thin film coated quartz, prepared by pyrolysis for 30min.

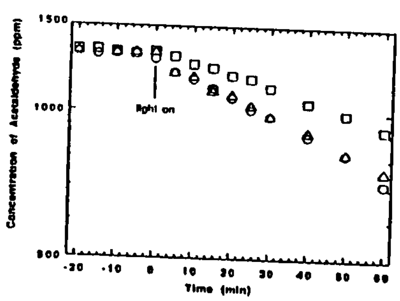

Figure 4 Photodegradation of acetaldehyde. TiO_2-coated quartz prepared by pyrolysis for 30min(O), TiO_2-coated SLG prepared by 60min(□), TiO_2-coated SiO_2/SLG prepared by 60min(Δ) Light Intensity at the film was 1.2mW/cm^2, 1.5L pyrex vessel.

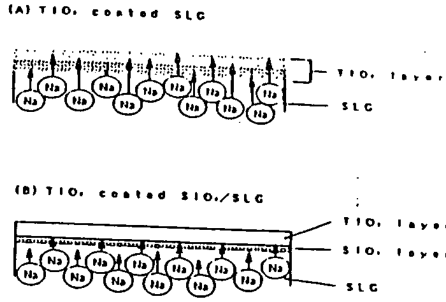

Figure 5 Schematic drawing of SiO_2 layer effect.

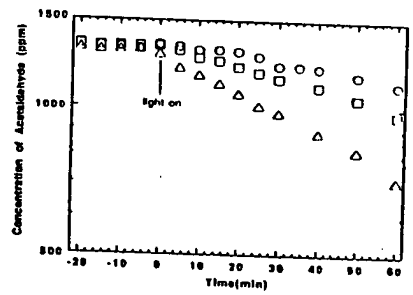

Figure 6 Photodegration of acetaldehyde. TiO_2-coated SiO_2/SLG prepared by 10min(O), 30min(□) and 60min(Δ). Light intensity at the film was 1.2mW/cm^2. 1.5L pyrex vessel.

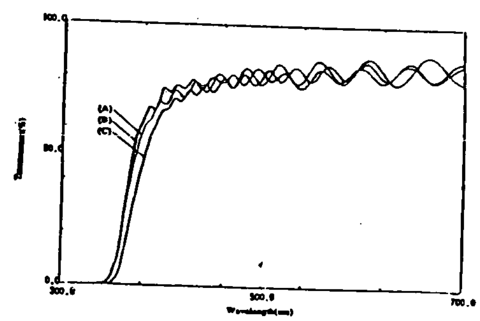

Figure 7 UV-Vis transmission spectrum of TiO_2-coated quartz prepared by 30min pyrolysis(A), TiO_2-coated SLG prepared by 60min(B) and TiO_2-coated SiO_2/SLG prepared by 60min.

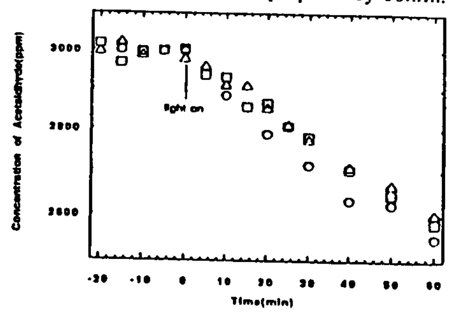

Figure 8 Photodegradation of acetaldehyde. P-25 powder(O).TiO_2-coated SiO_2/SLG prepared by 60min was irradiated from the front side(□) and reverse side(Λ). Light intensity at the film was 1.2mW/cm^2, 1.5L pyrex vessel. TiO_2-coated material has 25cm^2 (5cm x 5cm) of area.

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平成７年度研究報告書

1996年6月発行

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